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Diels-Alder-based thermo-reversibly crosslinked polymers: Interplay of crosslinking density, network mobility, kinetics and stereoisomerism

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ABSTRACT

Polymers crosslinked through thermo-reversible furan/maleimide Diels-Alder chemistry have been widely explored, since they stand as an ingenious design for reprocessable and self-healing thermosets and elastomers. For these polymeric products, crosslinking density plays a key role on the polymer thermo-reversibility. However, how this degree of network interconnectivity influences the kinetics of thermal reversibility has not yet been addressed. In order to tackle this problem, furan-grafted polyketones crosslinked by a bi-functional maleimide were prepared with different ratios between maleimide and furan groups. The thermo-reversible dynamics of the prepared polymers were then studied by rheology and differential scanning calorimetry. Here we show that, the thermo-reversible process occurs faster and at lower temperatures in polymers with lower crosslinking densities. Network mobility is responsible for this effect. It allows the formulations to rearrange their polymer network differently through the heating-cooling cycles. The results also indicate that the crosslinking density rather than the stereoisomerism of the Diels-Alder adducts plays a larger role in the reversible behavior of the system. Additionally, the thermo-reversible features of the polymer were shown to be dependent on its thermal history. This work impacts the development of reprocessable and self-healing crosslinked polymers, and the design of the corresponding reprocessing and healing procedures.

1. Introduction

During the last few decades, a rising state of environmental awareness has driven an immense amount of effort worldwide on developing eco-friendly polymers [1–4]. In this regard, thermosets and elastomers have received much attention [2,5], since they are widely used in a broad range of applications but cannot be easily reprocessed [5]. Ironically, the lack of reprocessability of these polymer products is caused by the same key structural feature that grants them superior mechanical properties, thermal stability, and solvent resistance (broadly compared to thermoplastics), i.e. their crosslinked polymeric network [5]. Such an interconnected network implies that the polymer cannot be melted upon heating and, therefore, it cannot be reprocessed. To overcome this drawback thermosets and elastomers are being designed with reversible linkages between the polymer backbones so that the system can be linked and cleaved at will by triggering this reversible process through an external stimulus. As a result, these reversibly

crosslinked polymers can be reprocessed.

Heat has been widely explored as a practical stimulus in order to trigger the reversible crosslinking process. Controlling the system temperature implies controlling the equilibrium between the chemical species involved in the (de)crosslinking process. Perhaps the best explored reaction for this purpose is the Diels-Alder diene/dienophile [4 + 2] cycloaddition (DA) [2,5]. The reaction has been widely used in the development of thermo-reversible crosslinked polymers (TRCP), and many different diene/dienophile combinations have been explored. Nonetheless, the furan (Fu)/maleimide (Ma) DA adduct is likely to be the most commonly studied pair (Fig. 1). This system has received intense attention because the adduct is formed and decoupled at practical and relatively low temperatures, about 60 °C and 110 °C, respectively [2]. The temperature range at which the process takes place depends on several factors, such as the polymer backbone [6–9], crosslinking density [10], crosslinking moieties [11,12], and macromolecular architecture [13,14]. These factors also influence the general properties

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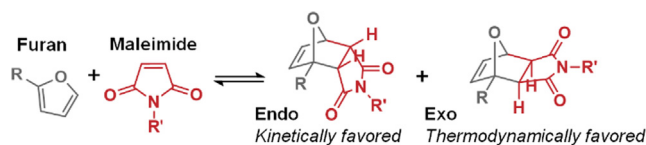


Fig. 1. Furan/maleimide adduct formation through Diels-Alder reaction (two possible stereoisomers are formed).

of the materials, making them highly tunable regarding their processing temperatures and mechanical performance [6–15].

Reversible crosslinking strategies may also come along with self-healing properties. Research on such self-healing polymers has been a hot topic for over two decades, since they stand as an ecofriendly alternative for substantially extending the lifetime of polymeric products through healing cycles [16]. The healing ability lies in the fact that such interconnected networks cleave upon heating, allowing the polymers to flow and fill up micro-cracks, and subsequently recover their cross-linked state when cooled. Thus, network mobility plays an important role in the healing process [16–18].

Not surprisingly, several studies of the crosslinking kinetics of these materials have been published [2,19–23] which provide valuable information about the changing system dynamics. They also provide quantitative kinetic parameters that allow predicting the speed at which a given process will take place under certain conditions. In these reports, the determined activation energies range approximately from 10–60 and 40–120 kJ/mol for DA and *retro*-DA, respectively (based on Fu/Ma reversible chemistry). The variations between these values within each range may arise from the fact that each report concerns different systems with many variables involved: chemical structure of the building-blocks, crosslinking density, chain mobility, polymer architecture, method used to follow the kinetics, and others. Recently, Cuvellier and coworkers [23] reported kinetic parameters for a polymer system which distinguished between the formation and cleavage of both DA stereoisomers. As expected, the endo adduct was shown to have a lower activation energy than its exo counterpart. Therefore, the former is favored kinetically while the latter thermodynamically.

Even though TRCP based on Fu/Ma chemistry have received intense attention, the effect of crosslinking density over the (de)crosslinking kinetics has not yet been systematically addressed. Here we prepared furan-grafted polyketones (Fig. 2a) crosslinked by a bi-functional maleimide (Fig. 2b) and investigate how the crosslinking density influences the kinetics of the thermo-reversible process. The polymer was selected based on the green features of this system [24–28], its self-healing capabilities [15], and the fact that these polymers are very easy and

safe to synthesize and process [10,25,27,29–33]. Formulations with different ratios between Ma and Fu groups (thus, crosslinker and Fu-grafted polymer) allowed us obtaining samples with different crosslinking densities. Correct preparation of the TRCP was checked by Fourier transform infrared spectroscopy (FTIR). Rheology and differential scanning calorimetry (DSC) measurements were used to monitor the DA thermo-reversible dynamics. Finally, based on the results, qualitative information regarding the kinetics of the thermo-reversible process, adduct stereochemistry and metastability is discussed throughout this work.

2. Experimental section

2.1. Materials

Different perfectly alternating polyketones were prepared as described by Drent and coworkers [34]. They differed in the relative ethylene and propylene content in the formulation: 0% ethylene content (Pk0, M_w : 1690 g/mol) or 30% ethylene content (Pk30, M_w : 2687 g/mol). The rest of the materials were acquired from Sigma-Aldrich: furfurylamine (used when freshly distilled), 1,1'-(methylenedi-4,1-phenylene)bismaleimide, and chloroform (HPLC grade).

2.2. Sample preparation

The TRCP were prepared as previously reported in detail by Toncelli and coworkers [10]. The two polyketone backbones (Pk0, Pk30) were initially grafted through the Paal-Knorr reaction with furfurylamine. Half of the active dimeric units were functionalized with furan groups for the two polymers (corroborated by elemental analysis, Euro EA) (Table SI). The grafted polyketones were then crosslinked with different amounts of the aromatic bismaleimide in order to achieve TRCP with different crosslinking densities. Four ratios between Ma and Fu groups were used: 0.3, 0.4, 0.5 and 0.7 (Table 1). The materials were named according to their respective polyketone backbone and ratio between the active groups (e.g. Pk0-Ma/Fu 0.3, was prepared using Pk0 and a Ma/Fu ratio of 0.3). FTIR spectroscopy was then used to characterize the TRCP and confirm their correct preparation (Shimadzu IRTracer-100).

2.3. Rheology

The TRCP were ground and placed into a cylindrical mold (8 mm diameter \times 1.5 mm thick). The samples were then molded for 20 min at 40 bar and 120 °C. The thermo-mechanical behavior of each sample

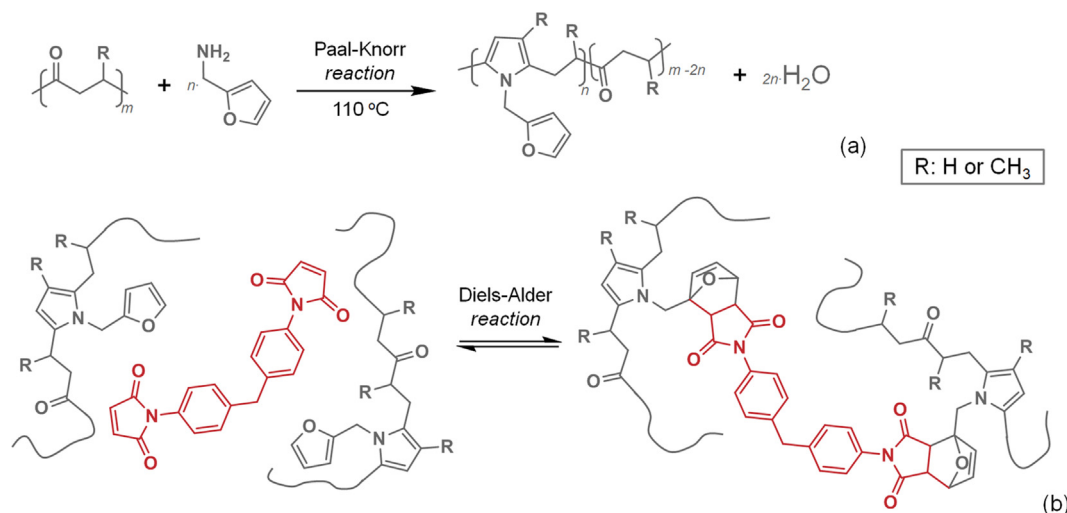


Fig. 2. (a) Furan functionalization of polyketones through Paal-Knorr reaction. (b) Fu/Ma DA thermo-reversible equilibrium of the system.

Table 1
Crosslinking of the furan-grafted polyketones with bismaleimide.

Sample name	Fu-grafted polyketone/g	Bismaleimide/g	Fu moieties/ $\text{mmol}\cdot\text{g}^{-1}$	Ma moieties/ $\text{mmol}\cdot\text{g}^{-1}$	Molar ratio: Ma/Fu
Pk0-Ma/Fu_0.3	5.80	0.82	2.5	0.69	0.28
Pk0-Ma/Fu_0.4	6.39	1.17	2.4	0.86	0.36
Pk0-Ma/Fu_0.5	6.02	1.61	2.3	1.2	0.52
Pk0-Ma/Fu_0.7	6.00	2.10	2.1	1.4	0.65
Pk30-Ma/Fu_0.3	9.99	1.42	2.4	0.69	0.29
Pk30-Ma/Fu_0.4	10.00	1.82	2.4	0.86	0.36
Pk30-Ma/Fu_0.5	9.74	2.59	2.2	1.2	0.55
Pk30-Ma/Fu_0.7	8.54	2.95	2.1	1.4	0.67

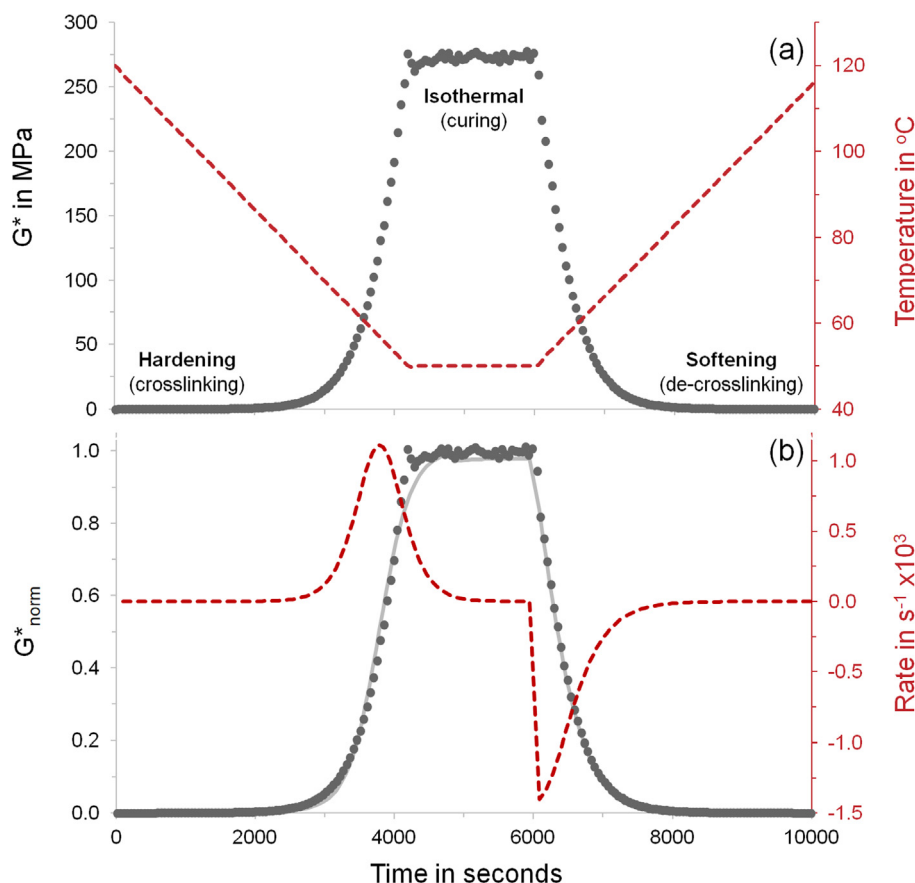


Fig. 3. Experimental design (e.g. Pk0-Ma/Fu_0.3, 1 K/min). (a) Complex modulus (gray circles) and temperature (red dashed line) vs. time. (b) Normalized thermo-mechanical properties (G^*_{norm} , gray circles) vs. time, along with the fitting (gray solid line) and its derivation (hardening and softening rates, red dashed line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was followed using a rheometer (Discovery HR-2, TA Instruments). As depicted in Fig. 3a, temperature scans from 120 °C to 50 °C were performed, followed by isothermal curing conditions (promoting DA crosslinking), and a final temperature sweep until 120 °C. The experiments were performed in oscillation mode with 0.2% strain, 1 Hz, and 10 N of axial force using an 8 mm geometry (0.2% strain was previously checked to be under the polymers linear viscoelastic plateau). TRIOS software was used to run the measurements and monitor the changes on the complex modulus (G^*). Each sample was measured using three different heating rates: 1, 3, and 5 K/min.

The thermo-mechanical profiles of the samples were normalized as shown in Eq. 1, where G^*_{min} is the complex modulus when the materials state is softest, and G^*_{max} , when the modulus is at its maximum. Therefore, G^*_{norm} values close to zero indicate that the network is practically de-crosslinked, while values tending to 1 imply the highest crosslinking scenario (Fig. 3b).

$$G^*_{norm} = \frac{G^* - G^*_{min}}{G^*_{max} - G^*_{min}} \quad (1)$$

In order to reduce the plot noise and allow studying the softening

and hardening rate (dG^*_{norm}/dt), the tangent hyperbolic fit shown in Eq. 2 was used (where P_i values are the best fit parameters). Then, from this fit, the softening and hardening rates were determined as the first derivative of Eq. 2 (Fig. 3b).

$$G^*_{norm} = P_1 + P_2 \cdot \tanh(P_3 \cdot \text{time} + P_4) \quad (2)$$

2.4. Differential scanning calorimetry

DSC experiments were carried out using a TA-Q1000 V9.8 Build 296. All samples (ground polymer) were weighed (5–10 mg) into aluminum pans. The measurements were carried out under nitrogen flow (50 ml/min). The following temperature program was used for the analysis: using a temperature ramp of 10 K/min, the polymer was heated from 20 up to 170 °C, then cooled down back to 20 °C (stabilized there for 5 min) and then the final temperature was again ramped up to 170 °C.

The resulting DSC plots were mathematically treated in order to correct the baseline. The following s-shaped polynomial model was applied to the raw data (where P_i values are the best fit parameters)

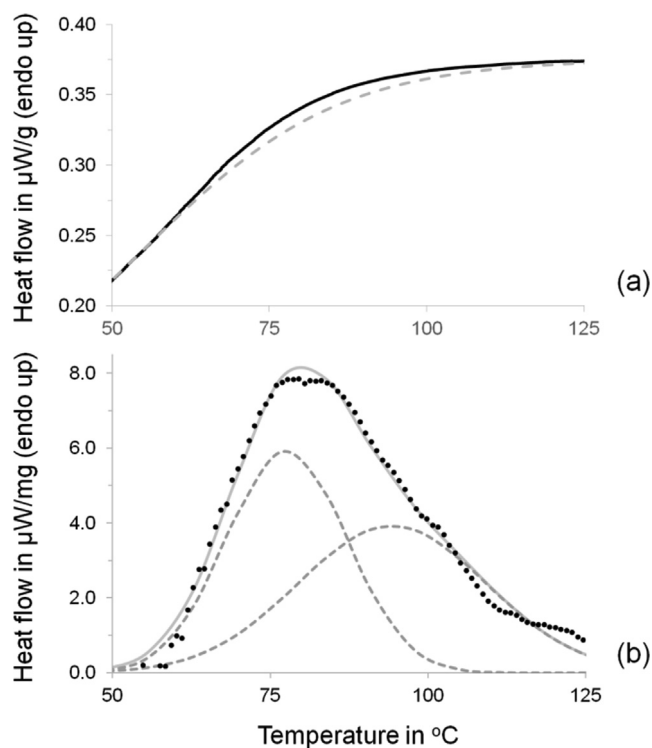


Fig. 4. (a) Measured data for Pk0-Ma/Fu_{0.3} (black solid line) and its corrected baseline (gray dashed line). (b) Fitting (gray solid line) and deconvolution (gray dashed line) of the corrected data (black points).

(Fig. 4a).

$$y = P_1 + \frac{P_2}{1 + e^{-P_3(x-P_4)}} \quad (3)$$

After the baselines were corrected, the plots were deconvoluted using Eq. 4; where n is the number of the deconvoluted peaks, A is the peak amplitude, 2σ is the full width at half maximum (FWHM), and μ is the temperature at which the peak maximum is located (Fig. 4b).

$$y = \sum_{i=1}^n \frac{A_i}{\sigma_i \sqrt{2\pi}} \cdot e^{-\frac{(x-\mu_i)^2}{2\sigma_i^2}} \quad (4)$$

3. Results and discussion

3.1. Sample preparation

The synthesis and characterization of the TRCP prepared in this work have already been fully described in the literature [10,11,27,35]. Supported by previous works, we confirmed the correct preparation of the materials by FTIR. We found similar fingerprints for the samples prepared here (Fig. 5) and the ones from the literature.

3.2. Thermo-reversibility

We prepared DA-based TRCP and explored how the crosslinking density affects the kinetics of the (de)crosslinking process. The main results, obtained by rheological measurements, are shown in Fig. 6. These measurements allow monitoring how the mechanical properties of the TRCP change through temperature ramps. The changes are caused by a simultaneous effect of the (de)crosslinking process of the interconnected network and the temperature-dependent mobility of the polymers linear chain segments. The plots show pronounced changes in the mechanical properties that are sharper (i.e. with higher softening and hardening rates) and occur at lower temperatures for the samples

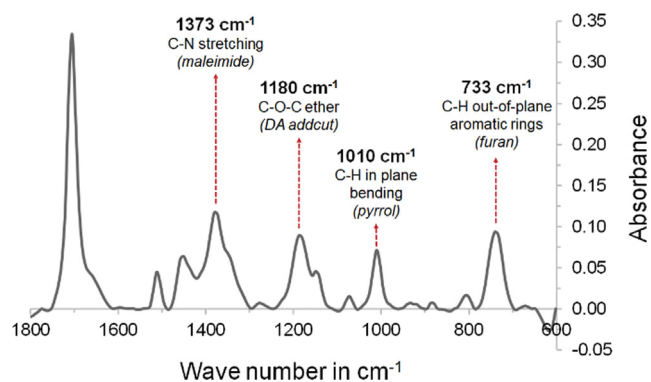


Fig. 5. FTIR fingerprint region of Pk0-Ma/Fu_{0.3} with the most important signals assigned.

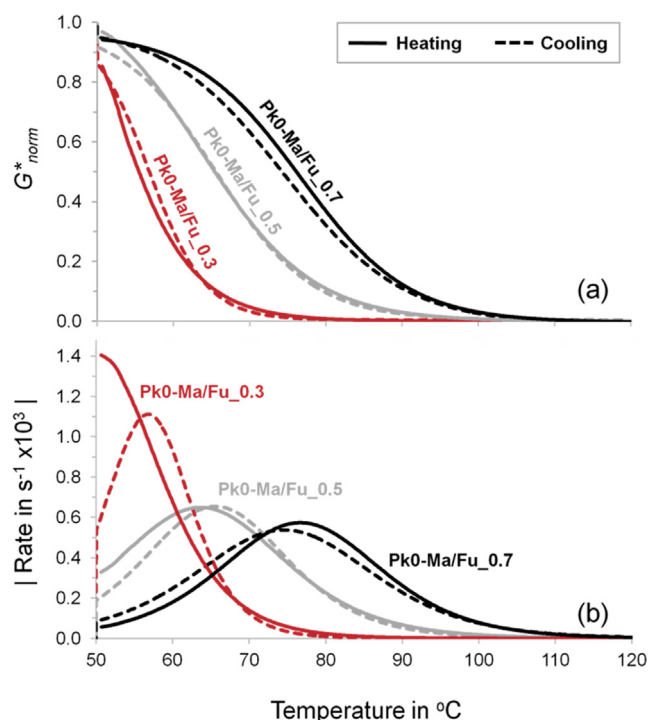


Fig. 6. (a) G^*_{norm} and (b) softening and hardening rates versus temperature. Solid and dashed lines represent heating and cooling processes, respectively. For simplicity, only experiments performed using Pk0-based polymers and temperature ramps of 1 K/min are shown (also only three of the four crosslinking densities are plotted). Nevertheless, this set of experiments demonstrates the trends observed for the rest of the analyzed samples at all heating rates (Fig. S1-2) (the raw data can also be seen in Fig. S3).

with less interconnected systems (lower Ma/Fu ratios). These features can be explained by the interplay of the polymer crosslinking density and network mobility as depicted in Fig. 7. Linear chain segments present higher mobility when the distance between the crosslinking points is larger so that the system is less interconnected, as is the case of samples with lower Ma/Fu ratio. This higher mobility enables these segments to reaccommodate more easily, thus, when the DA adducts decouple, there is a lower chance for the Ma and Fu moieties to re-encounter and form the adducts again. Consequently, the thermo-reversible process occurs faster. In this scenario, the systems with lower mobility (higher Ma/Fu ratios) would not only (de)crosslink more slowly, but would require higher temperatures to do so since the linear chain segments need enough energy to overcome their mobility restrictions.

From Fig. 6 it is also notable that different thermo-mechanical

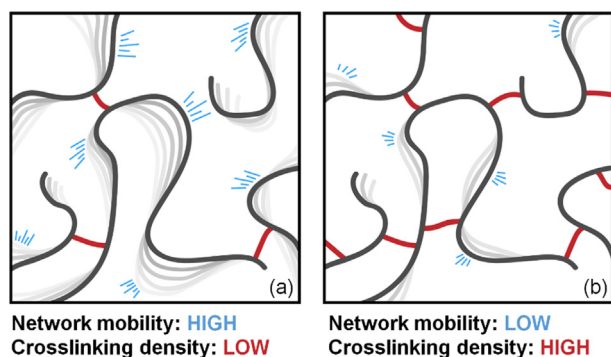


Fig. 7. Sketch of the network mobility in terms of the crosslinking density. Polymer systems with less crosslinking points have longer linear chain segments between crosslinks, therefore, the mobility of such segments is less restricted.

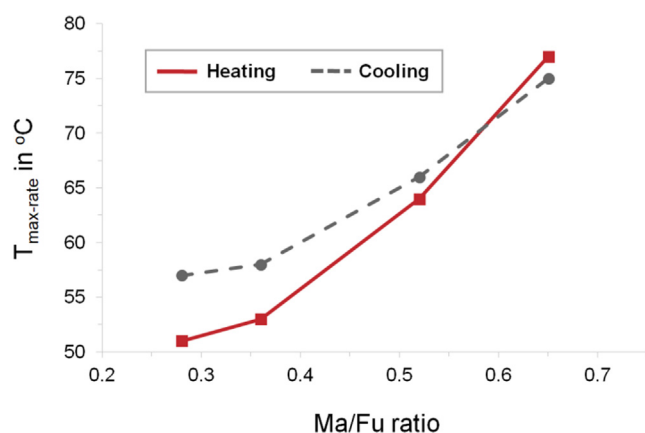


Fig. 8. $T_{\max\text{-rate}}$ against Ma/Fu ratio. For simplicity, only experiments performed using Pk0-based polymers and temperature ramps of 1 K/min are shown.

profiles are observed for cooling and heating. Fig. 8 displays the temperatures at which each hardening and softening maximum rates are located ($T_{\max\text{-rate}}$). The plots show how low-Ma/Fu-ratio formulations present their maximum hardening rate at higher temperatures than their maximum softening rate, while is the other way around for high-Ma/Fu-ratio formulations. This hysteresis supports the interplay of network mobility and crosslinking density discussed above. In systems with high network mobility, it is relatively easy for Ma and Fu groups to meet and couple or to get further apart as adducts decouple. Therefore, both the hardening and softening processes occur early during their temperature ramps, so that $T_{\max\text{-rate}}$ tends to be higher when cooling than when heating. On the other hand, in systems with mobility restrictions, it is not that easy for the reactive groups to find each other and react or to avoid forming the adduct again when being cleaved. Thus, both the hardening and softening process get delayed through their respective temperature ramps. Consequently, $T_{\max\text{-rate}}$ tends to be lower when cooling than when heating.

Fig. 9 shows the heating profiles obtained by DSC. The thermo-reversible process is followed by the heat generated by the cleavage of the DA adducts. The plots present the same trend observed in the rheological experiments, i.e. the decrosslinking taking place at higher temperatures for formulations with higher Ma/Fu ratios (due to their lower network mobility). However, the two techniques are monitoring different processes since the system is crosslinked by linear bi-functional Ma molecules (Fig. 2b). This implies that only the cleavage of one of the DA-adducts per bismaleimide molecule alters the number of crosslinks. Therefore, rheology measurements follow the actual decrosslinking process, while DSC keeps track of every adduct getting decoupled. Consequently, the thermal profiles obtained by the two techniques

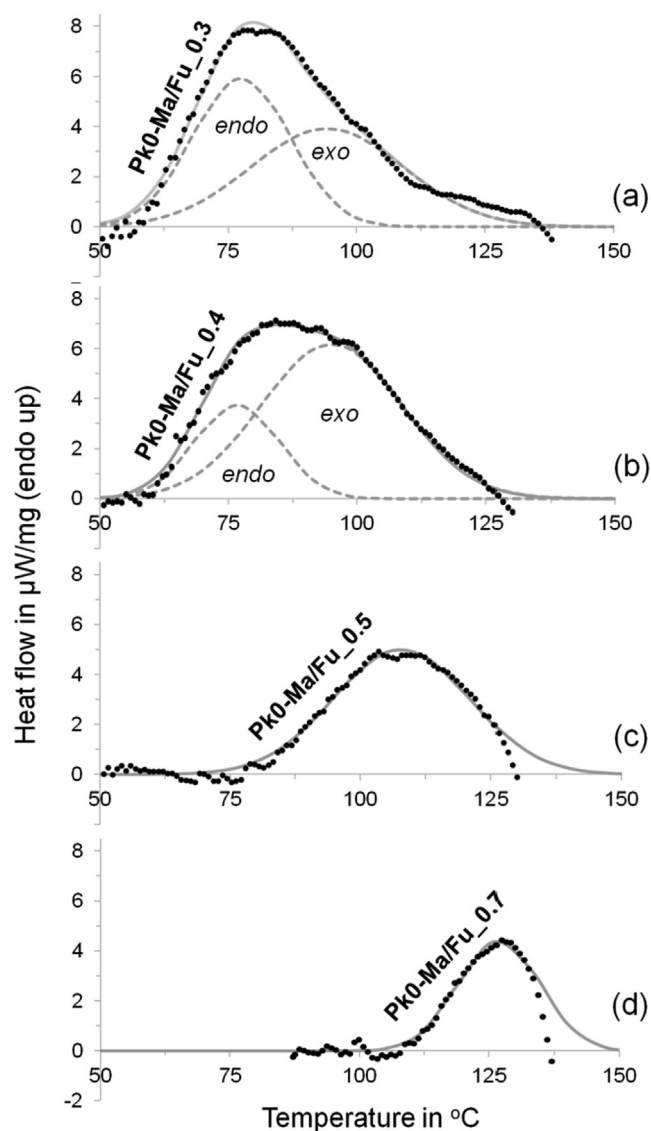


Fig. 9. DSC plots of Pk0-based formulations. Experimental data plotted as dots; best fit, as a solid line; and the deconvolution of the fit, as dashed lines. Only Pk0-based plots are shown (Pk30-based presented on Fig. S4).

show notable differences in the temperatures at which the processes take place. For instance, formulation PK0-Ma/Fu_{0.5} starts showing a decreasing modulus already at 50 °C, while its heat flow does not change up to 70 °C. The same effect has been observed in reports on different DA-based TRCP [27,36,37].

Fig. 9a–b also shows a best fit attributed to two different processes. In the literature, these two endotherms are attributed to the reactions of the possible DA stereoisomers [10,12,23,36,38–41]. From the two adducts, the exo isomer is the one that cleaves at higher temperatures. There is some variation regarding the reported temperature at which these two stereoisomers react. For some systems, the difference in the temperature at which each of the adducts react in bulk can be as large as 30–40 °C [12,23], while in others, the difference is smaller, and the two endotherms overlap [10,38]. For our TRCP system, the latter scenario seems to be the case. In this system, DSC results suggest that formulations with more network mobility present a higher ratio between endo and exo adducts. This observation might be explained by the fact that TRCP with more network mobility present their thermo-reversible features at lower temperatures. As a result, there is less energy in the system and the stereoisomer with the lowest activation energy is mostly formed (endo). Something similar occurs the other

way around; systems with less mobility react at higher temperatures, therefore there is more energy to overcome the higher activation energy required to obtain the most thermodynamically stable adduct (exo).

As seen in Fig. 9, the formulations with lower network mobility (Pk0-Ma/Fu_0.5 and Pk0-Ma/Fu_0.7) are not fitted with the two overlapping endo/exo endotherms. Instead, the heat flow declines sharply after 130 °C. This feature prevents a correct fitting and also indicate that an exothermic reaction has taken place (probably maleimide homopolymerization [42,43]). Such an exothermic event would also explain why the plots for samples with higher Ma/Fu ratios (thus, with more DA adducts) present lower enthalpies, as can be deduced from the smaller area under the DSC curves.

3.3. Network mobility, stereoisomerism and kinetics

In order to assess whether the endo/exo ratio has an impact on the (de)crosslinking kinetics and general behavior of the thermo-reversible polymer network, an additional experiment was performed. Pk0-Ma/Fu_0.3 was explored, as it consists of the formulation with the highest endo/exo ratio. The reason behind this selection is that the ratio between stereoisomers can be shifted towards lower values (exo promotion) through annealing. The experiment consisted of several heating and cooling cycles to follow the thermo-mechanical profiles and endo/exo ratios by rheology and DSC, respectively (Procedure S1). Fig. 10 shows the results (for simplicity, only the heating ramps are shown). First, the material was exposed to three heating-cooling cycles at 5 K/min. As usual, the very first heating cycle was done for erasing the polymer thermal history and the corresponding curve is not shown. The two following heating cycles (2nd–3rd) establish the basis of how the material behaves under the set conditions. They clearly indicate the reproducibility of the material behavior, as both curves are very similar. Before the 4th heating cycle (also at 5 K/min), a much slower cooling rate was used (0.2 K/min) for annealing. As an outcome, DSC endotherms increased considerably for both stereoisomers, with heat flow values over 2–3 times higher than before the annealing. Contrary to the initial hypothesis, the annealing process did not selectively promote the production of the most thermodynamically stable adduct

(exo). The process did increase the amount of exo adducts in the system, but also the endo ones. The outcome is reflected in the thermo-mechanical profiles as the inflection point of the drop in modulus shifted towards higher temperatures and the rate was reduced. Such observations are also seen in Fig. 6 for formulations with different Ma/Fu ratios, supporting the fact that the system simply became more cross-linked after the annealing. Other authors working with TRPC have reported as well on how the amount of endo and exo adducts change the crosslinking density, and subsequently the properties of the system [23].

Finally, two additional cycles (5th and 6th, also both at 5 K/min) were performed without the annealing step. The aim was to address whether the material behavior could be switched back to the ones seen before the annealing (as in 2nd–3rd cycles). The results show how, indeed, the sample properties are switched back, although only partially. This partial recovery is evidenced by the resulting curves, that overall, are an “in-between” scenario of the plots before and after the annealing. Such an intermediate state and its reproducibility (the last two cycles present very similar curves), indicates that the system is metastable and its thermo-reversible features depend on its thermal history. Therefore, thermal history can be considered as one of the many strategies for tuning the thermo-reversible process of these materials. Lastly, the maximum temperature reached in this set of experiments is relatively low (120 °C), hence, degradation of the polymer is not expected to take place and would not be responsible for the changes observed in Fig. 10. In a previous report, where the stability of these thermo-reversibly crosslinked polyketones [27] was explored, the material showed consistent thermo-mechanical profiles even after being reprocessed six times using compression molding (4 MPa at 120 °C).

3.4. Additional remarks

From a molecular perspective, it seems that the arrangement of the polymer network changes through the heating-cooling cycles. In each cycle, the system is prone to (1) experience interchangeability of the bonding moieties, (2) creep of chain segments, (3) interpenetration of the network, (4) changes in the crosslinking density and

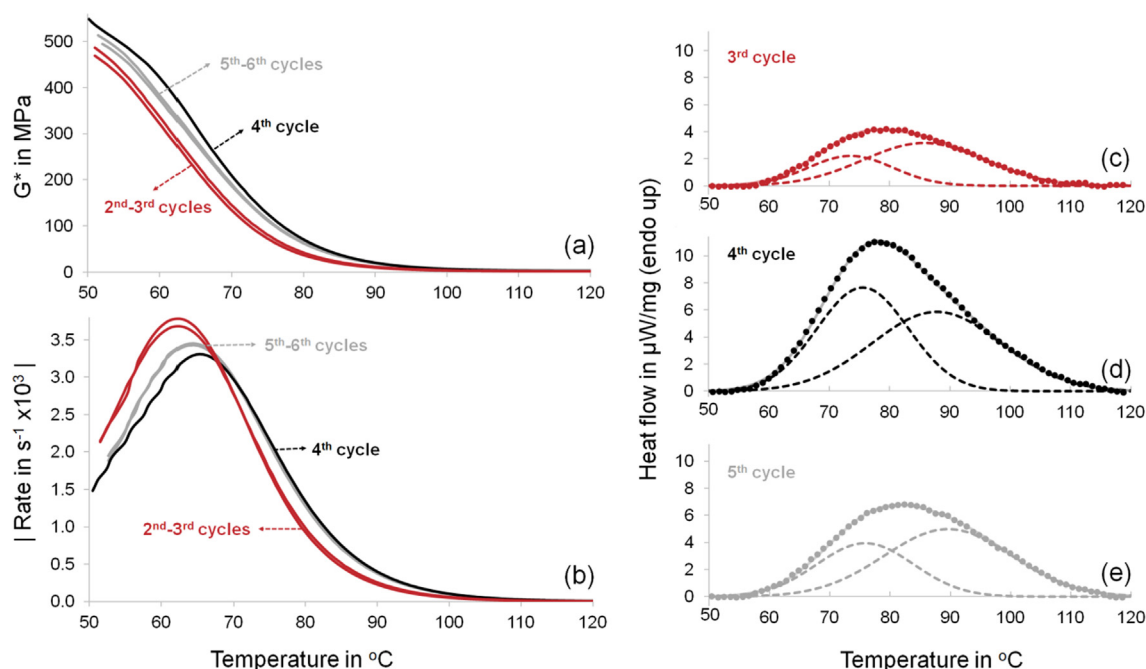


Fig. 10. Rheological and DSC measurements of Pk0-Ma/Fu_0.3. (a) G^* and (b) softening rate (dG^*/dt) versus temperature for several heating cycles. DSC experimental data plotted as dots; best fit, as a solid line; and the deconvolution of the fit, as dashed lines. The initial cycles are set in red; the 4th cycle (after annealing), in black; and the final cycles, in gray. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

stereochemistry of the adducts, and probably other alterations. All these rearrangements lead to the reprocessability and self-healing effect of TRCP. The extent of these rearrangements, and their impact on the polymer properties, depends on the crosslinking density of the system. These changes on the polymer network are also responsible for the changes in the thermo-reversible profiles when the samples are treated with different heating-cooling procedures.

In this work, polyketone-based TRCP were used. These are suitable model polymers since the furan-grafted chains undergo T_g ($< 30\text{ }^\circ\text{C}$ [11]) below the temperature range at which the DA thermo-reversible process takes place. Other TRCP that share this feature are expected to present a similar interplay of network mobility and thermo-reversibility, but not polymer systems with overlapping T_g and thermo-reversible temperature window.

This work shows how small differences in sample formulation, in terms of crosslinking density, influence the thermo-reversible features of DA-based TRCP. Such effects impact the development of reprocessable and self-healing thermosets and elastomers. The fact that thermo-reversible features depend on the thermal history of the polymers is crucial to consider when designing and implementing healing procedures for self-healing polymer products.

The network mobility explored here is conceived in terms of crosslinking density, while the mobility of the linear chain segments depends on their length. Similarly, packing of the chain linear segments may also influence network mobility and have the same effect on the thermo-reversible features. Fig. S5 seems to indicate just that (although, further investigation is needed). The plot shows the thermo-mechanical profiles of Pk0-Ma/Fu_0.3 and Pk30-Ma/Fu_0.3, i.e., samples with the same number of crosslinking points but differing in their polymer backbones. The Pk30-based formulation presents fewer methyl side groups on its backbone, therefore presents stronger van der Waals interactions between the chain segments and, thus, tighter packing. As a result, Pk30-Ma/Fu_0.3 has lower network mobility than Pk0-Ma/Fu_0.3 and presents the same differences in their plots as they would if the formulations differed on their Ma/Fu ratios.

The ratio between Fu and Ma groups was used here to control the network mobility through crosslinking density. As observed in Table 1, the Fu moieties were kept constant between formulations while the amount of bismaleimide was changed. Nevertheless, this excess of Fu moieties may also play a role in the network mobility. Araya-Hermosilla and coworkers [11] reported the glass transition temperature of a Fu-grafted polyketone to be $20\text{ }^\circ\text{C}$ higher than its alkyl-grafted counterpart (control). Therefore, the Fu groups present interactions along the polymer backbone, probably through π - π stacking with themselves or with the pyrrole rings. Nonetheless, these interactions are much weaker than the covalent bonds formed through the DA reaction and are expected to play a minor role in the overall network mobility after crosslinking. However, this excess of Fu groups might have an additional effect on the behavior of the systems. The fact that there are more Fu moieties available might facilitate the interchangeability of the DA adducts, thus, contributing to the faster kinetics of the thermo-reversibility observed for these formulations with lower crosslinking density.

4. Conclusions

Furan-grafted polyketones, thermo-reversibly crosslinked with linear bismaleimide, were prepared with different ratios between the polymer and the crosslinker. By this approach, formulations were obtained with different crosslinking density, and therefore, with different network mobility. The effect of crosslinking density on the kinetics of the thermo-reversible process was then explored. Our results show that the reversible process occurs faster and at lower temperatures in polymers with higher network mobility. Additionally, the results suggest that the number of crosslinking points play a more important role than the stereochemistry of the DA adducts on the thermo-reversible features of the system. The chemical and physical arrangement of the

polymer was shown to be metastable and depends on the thermal history of the material. This work impacts the development of reworkable and self-healing thermosets and elastomers, and the design of the corresponding reprocessing and healing procedures.

CRedit authorship contribution statement

Felipe Orozco: Conceptualization, Methodology, Investigation, Writing - original draft, Visualization. **Jing Li:** Methodology, Software, Investigation. **Unwana Ezekiel:** Software, Investigation. **Zafarjon Niyazov:** Investigation. **Lauren Floyd:** Investigation. **Guilherme M.R. Lima:** Investigation. **Jozef G.M. Winkelman:** Methodology, Software. **Ignacio Moreno-Villoslada:** Writing - review & editing. **Francesco Picchioni:** Conceptualization, Writing - review & editing, Visualization. **Ranjita K. Bose:** Conceptualization, Methodology, Writing - review & editing, Visualization, Supervision.

Data availability

The raw data required to reproduce these findings are available to download from <https://doi.org/10.17632/mf4x3txchk.1>. The processed data required to reproduce these findings are available to download from <https://doi.org/10.17632/mf4x3txchk.1>.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2020.109882>.

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